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(54) **Fiber-reinforced metallic composite material.**

(57) Improved fiber-reinforced metallic composite material comprises as a matrix a metal having a lower melting point and being chemically inactive (e.g. zinc, cadmium, indium, tin, thallium, lead, bismuth and polonium) or alloy thereof and as a reinforcement inorganic fibers of 15 to 70 % by volume, which is characteristic in that the metal alloy composing the matrix contains 0.01 to 10 % by weight of one or more metals of group IA or group IIA (except beryllium) in periodic table (e.g. lithium, sodium, potassium, rubidium, cesium, francium, magnesium, calcium, strontium, barium and radium). Said composite material has improved mechanical strength, and is useful as a material for various parts and apparatuses in various industrial fields such as aerospace, atomic power and automobile industries.

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FIBER-REINFORCED METALLIC COMPOSITE MATERIAL

This invention relates to a fiber-reinforced metallic composite material, more particularly to a fiber-reinforced metallic composite material comprising a matrix consisting of an alloy produced by incorporating one or more metals of group IA or group IIA (except beryllium) of the periodic table into a metal or alloy having a comparatively low melting point and being chemically inactive and inorganic fibers as a reinforcement, which has excellent mechanical strength (said fiber-reinforced metallic composite material being, hereinafter, referred to merely as "composite material").

There have recently been developed and utilized in various industrial fields some composite materials comprising an inorganic fiber (e.g. alumina fiber, silica fiber, silicon carbide fiber, boron fiber) and a matrix consisting of a metal such as aluminum, magnesium, copper, nickel, titanium, or an alloy thereof.

The metals or metal alloys as mentioned above have a high melting point and are chemically active, and hence, when these metals or metal alloys are reinforced with the inorganic fiber, a reaction proceeds at the interface metal-fiber which causes deterioration of the fibers. Hence, there cannot be obtained a composite material having excellent mechanical strength. It has been proposed to prevent such deterioration of the fibers by various means, for example, by treating the surface of the fibers with a coating agent, or by adding thereto a metal or alloy which is effective for preventing their deterioration.

When aluminum, magnesium, or titanium is used as a matrix metal, there can be provided a light weight composite material having high strength and high modulus. Besides, when copper, nickel, or titanium is used as a matrix metal, there can be provided a composite material having high strength and high modulus at a high temperature.

On the other hand, if metals having a comparatively low melting point and being chemically inactive (e.g. tin or zinc) which have a comparatively large specific weight but comparatively low strength are used as a matrix metal, their weight is a drawback, especially for the preparation of thick products or in a structure having support. This gives important design limitations. Likewise, metals having a comparatively low melting point and being chemically inactive (e.g. zinc, cadmium, indium, thallium, bismuth, polonium) which have low strength, give rise to design limitations like zinc and lead.

Under the circumstances, it has been desired to improve the strength of a matrix composed of a metal or an alloy having a comparatively low melting point and being chemically inactive (e.g. zinc, cadmium, indium, tin, thallium, lead, bismuth, polonium, or alloys thereof) by making a composite material with inorganic fibers. Although these metals used as a matrix are easily handled in view of the low melting point, they do not react with inorganic fibers because they are chemically inactive. Accordingly, the interfacial bond between matrix and inorganic fibers is extremely weak and external stress cannot be transferred via the matrix to the fibers, which causes firstly break of fibers and then pull-out of fibers. Therefore the desired composite material having excellent mechanical strength cannot be obtained.

In view of the above-mentioned situation, the present inventors have intensively studied as to an improvement of the strength of a matrix material composed of an inactive matrix and inorganic fibers and have found that for the inorganic fibers to exhibit maximum strength, shearing stress has to be induced at interface between the fibers and the matrix and forced to progress break along with the interface, and that for this purpose, it is effective to use as a matrix an alloy produced by incorporating one or more metals of group IA or group IIA (except beryllium) of the periodic table into a metal having a low melting point and being inactive as a matrix (hereinafter referred to as "matrix metal"). Thereby there can be obtained the desired composite material having excellent mechanical strength.

An object of this invention is to provide a fiber-reinforced metallic composite material wherein a metal or alloy having a low melting point and being chemically inactive is used as a matrix metal and the mechanical strength thereof is improved. Another object of the invention is to provide a fiber-reinforced metallic composite material using as a matrix an alloy of the matrix metal incorporated with one or more metals of group IA or group IIA (except beryllium) of the periodic table.

The composite material of this invention comprises as a matrix a metal or alloy having a relatively low melting point and being chemically inactive and as a reinforcement inorganic fibers in an amount of 15 to 70 % by volume. It is characterized in that the alloy composing the matrix contains 0.01 to 10 % by weight of one or more metals of group IA or group IIA (except beryllium) of the periodic table in addition to the matrix metal having a low melting point and being chemically inactive.

The inorganic fibers used in this invention include for example carbon fibers, silica fibers, silicon carbide fibers, boron fibers and alumina fibers. The inorganic fibers are contained in the composite material of this invention in an amount of 15 to 70 % by volume based on the whole volume of the composite material. When the amount of the fibers is less than 15 % by volume, the desired reinforcing effect can not sufficiently be achieved, and on the other hand, when the amount is over 70 % by volume, the strength of the composite material is rather lowered due to the mutual contact of fibers. The fibers may have any form, such as long fiber or short fiber, and any form of fibers can be used depending on the desired utilities of the product. The fibers may be used in one form or as a combination of different shapes. The fibers are applied to in various orientations, such as unidirectional crossplying or random orientation in order to give the desired mechanical strength and elasticity. Among these inorganic fibers, the most preferable fiber for achieving the desired reinforcing effect is an alumina fiber as disclosed in JP-B-13768/1976, i.e. an alumina fiber having an alumina (Al_2O_3) content of 72 to 100 % by weight, preferable 75 to 98 % by weight, and a silica (SiO_2) content of 0 to 28 % by weight, preferably 2 to 25 % by weight, and exhibiting substantially no reflection by X-ray diffraction due to the α-Al_2O_3 structure. This alumina fiber may optionally contain a refractory compound, for example, one or more oxide compounds of metals selected from lithium, beryllium, boron, sodium, magnesium, silicon, phosphorus, potassium, calcium, titanium, chromium, manganese, yttrium, zirconium, lanthanum, tungsten and barium, unless they do not affect the desired properties.

The matrix metal used in this invention includes metals having a comparatively low melting point and being chemically inactive, for example, zinc, cadmium, indium, tin, thallium, lead, bismuth, and polonium (provided that these alloys do not contain metals of group IA and group IIA (except beryllium) of the periodic table). The metals having a comparatively low melting point are metals having a melting point of 150 to 500 °C. The most suitable matrix metal may be elected in accordance with the conditions and circumstances where the products are used. For instance, for the purpose of using as a battery or for protection of irradiation of X-ray or γ-ray, lead is preferable. As an anode material for protection of electric corrosion, zinc is used. These metals used in this invention may optionally contain a small amount of impurities unless they do not give undesirable effects on the use of the product.

This invention is characterized by the use of a matrix of the above metals into which 0.01 to 10 % by weight of one or more metals selected from the metals of group IA and group IIA (except beryllium) of the periodic table are incorporated. Thereby the weak bond between the matrix and the fibers is improved to give a composite material having a strength close to the theoretical strength.

The metals of group IA and group IIA (except beryllium) of the periodic table include lithium, sodium, potassium, rubidium, cesium, francium, magnesium, calcium, strontium, barium and radium.

The mechanism of the improvement of the strength owing to the addition of the above-mentioned specific metals to the matrix metal may be assumed as follows.

The metals having a comparatively low melting point and being chemically inactive, for example, zinc, cadmium, indium, tin, thallium, lead, bismuth and polonium are inert to inorganic fibers, and hence, no reaction proceeds at the interface. However, when one or more metals of group IA or group IIA (except beryllium) of the periodic table are added to the matrix metals, these added metals are contained in a concentration higher than the average at the surface of the matrix metal. Thereby the added metals are present at a high concentration at the interface fiber-matrix and induce an interfacial reaction without deterioration of the fibers.

Hence the bonding strength at the interface is greatly enhanced.

When a composite material produced from a matrix of an alloy containing the additional metal is observed by a scanning electron microscope at a rupture cross-section thereof, the composite material has a stronger bonding at the fiber/matrix interface than a composite material obtained from a matrix of an alloy without the additional metal. It is also observed that the pull-out of the fibers is largely decreased and the bonding force at the interface fiber-matrix is increased.

The most suitable amount of the additional metal may vary depending on the kind of the inorganic fibers and/or the kind of the matrix metal, but the amount is usually in the range of 0.01 to 10 % by weight, preferably 0.1 to 5 % by weight, based on the weight of the matrix metal. When the addition amount is less than 0.01 % by weight, the desired improvement in the properties of the composite material cannot sufficiently be achieved, but on the other hand, when the amount is over 10 % by weight, the matrix metals lose their original excellent properties, that is, show a lowering of the corrosion resistance and a lowering of the tensile elongation, and further, the reaction of the fiber/matrix interface proceeds further to result in a deterioration of the fibers and thereby the composite material shows less improvement in the strength.

The metals of group IA or group IIA (except beryllium of the periodic table or alloys thereof can be incorporated into the matrix metal by various methods, for example, by a conventional method for producing alloys. For instance, a matrix metal is molten in a vessel at the air or under an inert atmosphere, and thereto are added the metals of group IA or group IIA (except beryllium) of the periodic table or alloys thereof, and the mixture is well stirred and then cooled.

The composite material of this invention can be prepared by various methods, for instance, (1) a liquid phase method (e.g. liquid metal impregnation method), (2) a powder metallurgy method (e.g. sintering or melt-bonding), (3) a deposition method (e.g. metal spraying, electrodeposition or flashing), (4) a plastic working method (e.g. extrusion or rolling), (5) a high-pressure casting method. The desired effect of this invention is particularly well exhibited in case of the liquid metal impregnation method (1) and the high-pressure casting method (5), but may also be exhibited in other methods (2) to (4).

The composite material of this invention shows an extremely large improvement of the mechanical strength in comparison with a product produced without the specific additional metals, and the production can be done with conventional apparatuses and methods without necessity of modification thereof. Accordingly, this invention is very useful for industrial production of excellent composite materials which are useful as a material for various parts and apparatuses in various industrial fields such as aerospace, atomic power and automobile industries.

This invention is illustrated by the following Examples.

Examples 1-3 and Comparative Examples 1-3

Pure zinc (purity, 99.97 %) (30 kg) is placed in a graphite crucible and is molten at about 600 °C. Strontium (purity, 99 %) (300 g) is added to the above vessel, and the mixture is well stirred with a carbon steel bar coated with mica flour on the surface thereof to produce an Zn-Sr(1.0 % by weight) alloy.

Alumina fibers (Al_2O_3 content: 85 % by weight, SiO_2 content: 15 % by weight, mean fiber size: 14 µm, tensile strength: 180 kg/mm^2, tensile modulus: 23,500 kg/mm^2, manufactured by Sumitomo Chemical Company, Limited, Japan) are used as an inorganic fiber. The fibers are arranged unidirectionally in a size of longitudinal length of 100 mm, horizontal length of 200 mm and a height of 6 mm. Separately, carbon fibers (mean fiber size: 8 µm, tensile strength: 370 kg/mm^2, tensile modulus: 23,600 kg/mm^2, manufactured by Sumika-Hercules, Japan) are arranged in the same size as the above alumina fibers. Besides, alumina short fibers (RG grade, manufactured by ICI, Al_2O_3 content: 96-97 %, SiO_2 content: 3-4 %, mean fiber size: 3 µm, tensile strength: 100-200 kg/mm^2, tensile modulus: 30,000-33,000 kg/mm^2) are formed in a paper-like material (thickness: 1 mm) and this material is cut in a size of longitudinal length of 100 mm and horizontal length of 200 mm and are laminated in a height of 6 mm. These fibers are heated at 600 °C in a nickel-chromium furnace. Only in case of carbon fibers, the heating is carried out while passing nitrogen gas through the furnace.

A plunger pressing mold is charged with the fibers which are previously heated, and the above Zn-Sr-(1.0 % by weight) alloy molten at 600 °C is poured into the cylinder and then pressed at 500 kg/cm^2 with a plunger, and thereby the alloy is coagulated under pressure to obtain plate-shaped composite materials.

For comparison purpose, composite materials are prepared by using pure zinc (purity, 99.97 %) alone as a matrix in the same manner as described above.

Test samples for tensile strength were prepared from the above composite materials. The tensile strength was measured at room temperature by a method as defined in ASTM E8-82. The results are shown in Table 1.

Table 1

No.	Inorganic fibers	Matrix	fiber content (% by volume)	Tensile strength (kg/mm^2)
1	Alumina fibers	Zn-Sr(1.0 %)	50	120
2	Carbon fibers	Zn-Sr(1.0 %)	50	150
3	Alumina short fibers	Zn-Sr(1.0 %)	15	60
Comp. Ex. 1	Alumina fibers	Zn	50	50
Comp. Ex. 2	Carbon fibers	Zn	50	70
Comp. Ex. 3	Alumina short fibers	Zn	15	20

Examples 4-6 and Comparative Examples 4-6

Pure lead (purity, 99.9 %) (30 kg) is placed in a graphite crucible and is molten at about 450 °C. Cesium (purity, 99.9 %) (30 g) is added thereto, and the mixture is treated in the same manner as described in Examples 1-3 to prepare a Pb-Cs(0.1 % by weight) alloy. The same fibers as used in Examples 1-3 are each formed in products having the same size as in Examples 1-3, and plate-shaped composite materials are prepared under the same conditions as described in Examples 1-3 except that the heating temperature of fibers is 400 °C (the carbon fibers are also heated in air) and the temperature of pouring of molten matrix metal is 400 °C.

For comparison purpose, composite materials are prepared by using pure lead (purity, 99 4 %) alone as a matrix in the same manner as described above.

Test samples for tensile strength were prepared from the above composite materials in the same manner as described in Examples 1-3. The tensile strength was measured at room temperature in the same manner as in Examples 1-3. The results are shown in Table 2.

Table 2

No.	Inorganic fibers	Matrix	fiber content (% by volume)	Tensile strength (kg/mm^2)
4	Alumina fibers	Pb-Cs(0.1 %)	50	110
5	Carbon fibers	Pb-Cs(0.1 %)	50	130
6	Alumina short fibers	Pb-Cs(0.1 %)	15	40
Comp. Ex. 4	Alumina fibers	Pb	50	40
Comp. Ex. 5	Carbon fibers	Pb	50	60
Comp. Ex. 6	Alumina short fibers	Pb	15	10

Examples 7-11

Pure zinc (purity, 99.97 %) (30 kg) is placed in a graphite crucible and is molten at about 600 °C. Five runs of such molten zinc are prepared.

To the molten zinc is added barium (purity, 99 %), lithium (purity 99 %), calcium (purity, 99 %), or magnesium (purity, 99.85 %), and the mixture is treated in the same manner as described in Examples 1-3 to prepare Zn-Ba(0.7 % by weight) alloy, Zn-Li(0.6 % by weight) alloy, Zn-Ca(0.7 % by weight) alloy, Zn-Mg(0.7 % by weight) alloy, and Zn-Mg (2.5 % by weight) alloy.

The same alumina fiber as used in Examples 1-3 is used as the inorganic fiber. The fibers are arranged unidirectionally in the same size as in Examples 1-3. Five runs of such a product are prepared. The fibers are heated at 600 °C in a nickel-chromium furnace as in Examples 1-3.

A plunger pressing mold is charged with the fibers which are previously heated, and the above Zn alloys molten at 600 °C is poured into the cylinder and then pressed at 500 kg/cm^2 with a plunger, and thereby the alloy is coagurated under pressure to obtain plate-shaped composite materials as in Examples 1-3.

Test samples for tensile strength were prepared from the above composite materials. The tensile strength was measured at room temperature in the same manner as in Examples 1-3. The results are shown in Table 3.

Table 3

No.	Inorganic fibers	Matrix	fiber content (% by volume)	Tensile strength (kg/mm^2)
7	Alumina fibers	Zn-Ba(0.7 %)	50	80
8	Alumina fibers	Zn-Li(0.6 %)	50	75
9	Alumina fibers	Zn-Ca(0.7 %)	50	95
10	Alumina fibers	Zn-Mg(0.7 %)	50	110
11	Alumina fibers	Zn-Mg(2.5 %)	50	70

Claims

1. A fiber-reinforced metallic composite material, which comprises as a matrix a metal having a relatively low melting point and being chemically inactive or an alloy thereof and as a reinforcement inorganic fibers in an amount of 15 to 70 % by volume, said metal alloy composing the matrix containing 0.01 to 10 % by weight of at least one metal of group IA or group IIA (except beryllium) of the periodic table.

2. The fiber-reinforced metallic composite material according to claim 1, wherein the metal alloy composing the matrix contains 0.1 to 5 % by weight of at least one metal of group IA or group IIA (except beryllium) of the periodic table.

3. The fiber-reinforced metallic composite material according to claim 1 or 2, wherein the metal of group IA or group IIA (except beryllium) of the periodic table is lithium, sodium, potassium, rubidium, cesium, francium, magnesium, calcium, strontium, barium or radium.

4. The fiber-reinforced metallic composite material according to any one of claims 1 to 3, wherein the metal having a relatively low melting point and being chemically inactive is zinc, cadmium, indium, tin, thallium, lead, bismuth or polonium.

5. The fiber-reinforced metallic composite material according to any one of claims 1 to 4, wherein the inorganic fiber is an alumina fiber having an alumina content of 72 to 100 % by weight and a silica content of 0 to 28 % by weight and exhibiting substantially no reflection by X-ray diffraction due to the α-Al_2O_3 structure.

6. The fiber-reinforced metallic composite material according to claim 5, wherein the alumina fiber contains a refractory oxide compound of lithium, beryllium, boron, sodium, magnesium, silicon, phosphorus, potassium, calcium, titanium, chromium, manganese, yttrium, zirconium, lanthanum, tungsten, and/or barium.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 88 11 1334

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	GB-A-2 081 353 (SUMITOMO CHEMICAL CO. LTD) * Claims 1-4 *	1,2	C 22 C 1/09
A	GB-A-2 080 865 (SUMITOMO CHEMICAL CO. LTD) * Claims 1-3 *	1,2	
A	EP-A-0 062 496 (SUMITOMO CHEMICAL CO. LTD) * Claims 1,2 *	5	
A	FR-A-2 297 255 (FIBER MATERIALS INC.) * Claim 1 *	1,4	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 27 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	13-10-1988	GREGG N.R.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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& : member of the same patent family, corresponding document